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TITLE: MAGNETIC REFRIGERATION: THE PROMISE AND THE PROBLEMS

AUTHOR(S): J. A. Barclay

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Los Alamos

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Magnetic Refrigeration: the Promise and the Problems

J. A. Barclay, Project Leader
Group P-10, MS-K764
Los Alamos National Laboratory
Los Alamos, NM 87545

ABSTRACT

Magnetic refrigeration uses the temperature- and field-dependence of the entropy of some magnetic materials to accomplish cooling. Because of the intrinsically high efficiency of the magnetization and demagnetization process and because of the potential for excellent heat transfer between solids and fluids, magnetic refrigerators promise to have higher efficiency than existing gas-cycle refrigerators. Many ground-based and space-based applications could benefit significantly from the cost savings implied by higher efficiency. Other attributes of these devices are high reliability and low volume and mass per unit cooling power. The development of these refrigerators is underway at several places around the world, including the Los Alamos National Laboratory. The progress to date has been encouraging but some problems have been clearly identified. The arguments for high efficiency and the problems that will need to be solved to achieve this goal are discussed.

INTRODUCTION

Important features of refrigerators include efficiency, reliability, lifetime, size, and mass. The efficient liquefaction of cryogens, such as liquid hydrogen, is important because the liquefaction cost is a significant fraction of their total cost. The costs of liquid nitrogen and liquid oxygen are also tightly coupled to the cost of refrigeration for air separation. At present, all of the refrigeration required to produce cryogens is provided by gas-cycle devices in which gas is compressed in one part of the cycle to reject heat from the gas and expanded in another part of the cycle to cool and eventually liquefy the gas.[1] Lifetime and reliability studies of refrigerators are limited to specific design tests, but several studies of efficiency as a function of cooling power of gas-based refrigerators for cryogens have been published, including compilations of mass and volume.[2-7] The main sources of inefficiency are the room-temperature compressors with their associated aftercoolers and the gas expanders. Generally, the compressors and expanders are the least-reliable components too. All of the efficiency studies agree that $\sim 35\%$ of Carnot efficiency is the best that is now possible, but then only for very large plants. For smaller machines, the fraction of Carnot efficiency can become very small, e.g., 1-W refrigerators generally operate in the range 2-8% of Carnot. One study[5] on liquid hydrogen indicates that no significant advances in liquefaction efficiency are probable by the year 2000 unless very large investments are made in research and development. Therefore, it is important to investigate other promising technologies to see if they offer higher efficiency with less investment. One such technology is magnetic refrigeration (MR). MR exploits the temperature and magnetic-field dependence of the magnetic entropy of some solid materials to extract heat from a low-temperature source and transfer it to a higher temperature sink. The temperature change associated with the application or removal of a magnetic field to an isolated sample is called the magnetocaloric effect. This paper presents several reasons why magnetic refrigeration offers significant promise and identifies some of the problems that must be overcome before this promise is realized.

FUNDAMENTALS OF MAGNETIC REFRIGERATION[8]

Any refrigeration system requires some mechanism to increase or decrease the entropy of a working substance. In addition, heat transfer at appropriate times during a cycle

is necessary. Further analysis of various magnetic refrigerator designs produces a list of the functions required to execute the thermodynamic cycles. A summary of functions in the basic magnetic cycle over a large temperature span such as 20 to 77 K is given below:

- magnetization of ferromagnets near the hot temperature to reject heat to a sink such as liquid nitrogen, by circulation of a heat exchange fluid, such as helium gas;
- regeneration of the magnetic material to cool it to near the cold temperature (20 K); this regeneration requires heat transfer between an external regenerative material or the magnetic material itself and a moving heat transfer fluid;
- demagnetization of the ferromagnet near the cold temperature to absorb heat from a load, such as hydrogen by circulation of a heat exchange fluid, such as helium gas; and
- regeneration of the magnetic material to warm it to near the hot temperature (77 K); as before, this regeneration requires heat transfer between a regenerator material and a moving heat transfer fluid.

The work for the magnetic cycle is provided by a motor working against the difference in forces during the magnetization and demagnetization. The cycle requires either moving the material or the magnet or some equivalent change. The rate of movement through the magnetic cycle is very slow compared to many gas cycles; ranging from ~0.1 Hz to ~1 Hz.

THE PROMISE OF MAGNETIC REFRIGERATION

Magnetic refrigeration is an unproven technology but it does have several attributes which make it worthy of development. The first and perhaps most exciting is the prospect of much higher efficiency than existing gas-cycle refrigerators or liquefiers. In general terms, this claim is based upon two arguements. First, the magnetization and demagnetization of a magnetic solid provides an entropy change that is reversible at low frequencies, such as 1 Hz which are the normal operating frequencies of magnetic refrigerators. Secondly, the heat transfer in magnetic refrigerators is between a solid and a gas, which is intrinsically better than gas-to-solid-to-gas, as is required in gas-cycle devices.

An analysis of the sources of inefficiency in magnetic cycles[9] clearly indicates that the biggest fundamental source of irreversibility in magnetic refrigerators is that due to heat transfer across a temperature difference in the regenerative parts of the

cycle. From reference 8, the rate of work of a magnetic cycle can be written as

$$\dot{W} = \dot{Q}_C\left(\frac{T_H}{T_c} - 1\right) + \frac{T_H\int \dot{W}_i\left(\frac{1}{T} - \frac{1}{T_H}\right)dT}{dT}$$

$$+ \frac{T_H\int \dot{q}_i\left(\frac{1}{T} - \frac{1}{T_H}\right)dT}{dT} + \frac{T_H\int \Delta\dot{S}_{IRR}dT}{\int dT}; \quad (1)$$

and the relative efficiency can be written as

$$n = \frac{\dot{Q}_C}{\dot{W}_{TOTAL}}\left(\frac{T_H}{T_c} - 1\right) . \quad (2)$$

where $\dot{Q}_C$ is the reversible cooling power, $\dot{W}_i$ is power added externally to move fluid, $\dot{q}_i$ is power introduced through heat conduction from the surroundings, and $\Delta\dot{S}_{IRR}$ is the rate of irreversible entropy production from different mechanisms. The irreversibility due to heat transfer across a temperature difference in the regenerative parts of the cycle was retained in the expressions above and a quantitative expression was evaluated, given as

$$\dot{W}_{TOTAL} = \dot{Q}_C\left(\frac{T_H}{T_c} - 1\right)$$

$$+ \frac{T_H\int_{T_c}^{T_H} \Delta\dot{S}_{IRR}\,dT}{\int_{T_c}^{T_H}} . \quad (3)$$

Following the analysis, the resultant efficiency expressions were written as

$$\frac{1}{n} = 1 + \frac{2\left(T_H - T_c\right)}{\left(N_{tu}^R + 1\right)\left(\Delta T_c\right)} \quad (4)$$

for the temperature range where the heat capacity of the magnetic solid is approximately constant. N_{tu}^R is the number of heat transfer units in the regenerative-cycle step and ΔT_c is the adiabatic temperature change at the cold end of the cycle. The hot and cold temperatures are T_H and T_c, respectively. When the solid heat capacity is a linear function of temperature, the efficiency expression becomes

$$\frac{1}{\eta} = 1 + \frac{2\left(T_H^2 - T_c^2\right)}{\left[T_c^2 - \left(T_c - \Delta T_c\right)^2\right]\left(N_{tu}^R + 1\right)} \quad . \quad (5)$$

The analysis in reference 8 shows that magnetic refrigerator spanning 4 K to 300 K can be considered in three ranges on the basis of regeneration. The range 4-20 K needs little or no regeneration, the range 20-150 K needs regeneration where the heat capacity of the working solid is approximately linear in T, and the range 150-300 K needs regeneration where the heat capacity is approximately constant. Projected efficiencies for several 4-20 K stages are $\approx 70\%$ of Carnot. Optimistic estimates of numbers for a magnetic refrigerator operating above 20 K are $N_{tu} \approx 500$ and $\Delta T_c \approx 15$ K. Substitution of these values into Eqs. (5) and (4) for the 20-150 K and 150-300 K range, respectively, gives η (20-150 K) = 81% and η (150-300 K) = 98%. When the efficiencies of the three stages are combined, the resultant efficiency is a very impressive 62% of Carnot for a 4.5-to-300 K magnetic refrigerator. For hydrogen liquefaction applications, the amount of cooling power at 4 K to maintain the liquid-helium for the magnets will be very small compared to the cooling power at and above 20 K. In this case, the potential efficiency for the example above approaches 30% of Carnot! Clearly, the other irreversibilities in the refrigerator will lower the efficiency but they should be small compared to the regenerative heat transfer irreversibility and so the overall efficiency is potentially extremely high compared to 35% or less for conventional systems.

THE PROBLEMS OF MAGNETIC REFRIGERATION

As with any new technology, there are some problems that must be solved in order to achieve the final result. The equations already presented pinpoint some of the problem areas. From Eq. (4) it is clear that the efficiency is strongly dependent upon the adiabatic temperature change ΔT_c. For gadolinium metal near its Curie temperature (290 K), the adiabatic temperature change is approximately 2 K per Tesla up to ~ 9 T for a upper limit of ~ 20 K. When intermetallic coumpounds of gadolinium are used to obtain the lower Curie temperatures, for example, GdNi at ~ 70 K, the adiabatic temperature change decreases because of the added nickel. Measured values[10] of the adiabatic temperature change for GdNi show about 12 K at 9 T right at the Curie temperature. Average ΔT's over a 20-30 K span about the Curie temperature are 25-40% less. Therefore, one problem is to find magnetic materials that have the largest possible adiabatic temperature changes.

Associated with the above problem is the reduction of the adiabatic temperature change by the thermal addenda of the structure containing the refrigerent. The problem reduces to generation of clever designs that can satisfy the structural demands and, at the same time, have extremely small thermal mass.

For ferromagnets near their Curie temperature, the adiabatic temperature change is almost linearly proportional to the field strength. Therefore, the largest practical magnetic field must be used to produce the largest adiabatic temperature change. For standard solenoids, made from readily available NbTi superconductor, 9T is an upper limit at 4.2 K, but fields above 10 T can be reached if the magnet is cooled to 1.8 K. If Nb3Sn is used as the superconductor, magnetic fields of 15 T can be obtained but at the expense of significant manufacturing difficulties. Magnetic refrigerator designs have been made that use racetrack and helmholtz or even more exotic-shaped coils. Because these coils have a poorer ratio of field at the center of the coil to field in the windings than for a solenoid, it is more difficult to achieve high fields in the working space. If shapes other than solenoids are needed, a development effort will be required to achieve magnets providing working fields of 9-10 T or higher.

Equation (4) also shows that the number of heat transfer units in the regenerative parts of the cycle strongly influences the overall efficiency. The N_{tu} is defined as $\sigma A_c / \dot{m} C_p$, where σ is the conductance between the solid and fluid, A_c is the surface area of the solid that the fluid contacts, $\dot{m}$ and C_p are the mass flow rate and heat capacity of the fluid, respectively. Because the conductance between the fluid and solid is intrinsically limited by the thermal conductivity of the boundary layer of fluid on the solid, the contact area has to be increased as much as possible to obtain the highest N_{tu}. Geometries such as tubes, sheets, and particles have very large surface areas per unit volume if the dimensions are carefully chosen. However, the N_{tu} can not be arbitrarily increased by increasing the contact area because the pressure drop also rises rapidly in geometries where the surface area is increased by making all of the flow channels very small. The longitudinal conduction of the geometry is also of importance in the design of efficient regenerators. The optimum balance of heat transfer, pressure drop, and longitudinal conduction in magnetic-material structures suitable for cyclic movement to execute a regenerative cycle is definitely one of the key problems in magnetic refrigeration.

The structural design is important because of the large forces between the magnetic solid and the magnetic field of the magnet. One of the problems that must be carefully addressed during the design is how to cancel the magnetic forces from one part of the cycle against those of another part of the cycle. For example, in a reciprocating design, the cylinder of magnetic solid is strongly attracted into the magnet during magnetization and slightly more strongly attracted by the magnet during demagnetization. The difference between these two large forces is the net force that provides the cycle work. If two cylinders are arranged so that the forces almost cancel, the structure separating the two cylinders must be designed to withstand the large compressive stress but not thermally short circuit the cylinders.

Two further problems that must be addressed are illustrated by the following expression for the rate of total refrigerator work, i.e.,

$$\dot{W}_{TOTAL} = \frac{\dot{W}_{REF}}{\eta_{drive}} + \frac{\dot{w}}{\eta_{pump}} , \qquad (6)$$

where $\dot{W}_{REF}$ is the rate of work from the refrigerator cycle, η_{drive} is the efficiency of the motor and drive providing the refrigerator work, $\dot{w}$ is the external work rate from the fluid pumps and η_{pump} is the pump efficiency. The pump work rate $\dot{w}$ is generally much lower than $\dot{W}_{REF}$ so the drive-motor and gear-mechanism efficiency is directly related to the overall refrigerator efficiency. Unfortunately, ordinary AC synchronous motors geared down to ~1 Hz have efficiencies near 25% of ideal which, would limit the refrigerator efficiency to 25% of Carnot. To achieve the high efficiency projected earlier, drive motor/mechanisms with 90-95% of ideal efficiency have to be developed. Efficient and reliable low-temperature pumps definitely have to be developed before magnetic refrigerators can achieve their potential long life and high reliability.

External heat exchangers are the last major problem area that must be considered, particularly into a multistage refrigerator. If every stage spanning ~40 K requires overlapping heat exchangers, the effect on the overall efficiency is very serious. Ideally, new staging concepts will eliminate separate heat exchanges for each material and require only the cold source exchanger and the hot sink exchanger.

CONCLUSION

The potential elimination of the compressor and after-cooler of a conventional gas-cycle liquefier and the possibility of excellent regenerative heat transfer gives MR promise for much higher efficiency than gas cycle devices. Higher efficiency has many cost benefits for large-scale ground based applications, such as liquefaction of hydrogen for shuttle flights. Space-station applications, such as cryogen fuel storage and handling, will also need efficient refrigerators to help reduce system costs. High efficiency is one of the most exciting features of MR, but because of the low speed and relatively few moving parts, the reliability and lifetime of these devices also promises to be excellent. For some space missions, this feature is even more important than the efficiency. Designs with clearance seals and hermetic power couplings are possible and should add to the reliability. Bearing lifetime will have to be considered but balanced mechanical loads should avoid serious limitations here.

Two further desirable features of MR are the potential for smaller mass and volume per unit cooling power. These features result from using a solid working material instead of a gas. The magnet/dewar combination is more compact than the compressor system when all but very small cooling powers are required.

While many desirable features are possible if magnetic refrigerators are successfully developed, it is apparent that a significant number of problems must be solved before success is attainable. The materials and heat transfer problems present certain limitations that must be carefully handled in any optimized design. The pumps, drive motors, and magnets present engineering problems that must be overcome. At this time, the outlook for successful development of MR is excellent but a great deal of work needs to be done.

NOMENCLATURE AND UNITS

A_c contact area (m^2)

C_p fluid heat capacity (J/hgK)

$\dot{m}$ fluid flow rate (kg/s)

N_{tu}^p number of heat transfer units in regenerator (dimensionless)

$\dot{q}_j$ rate of heat flow into refrigerator from external sources via conduction, radiation, etc.

$\dot{Q}_C$ cooling power at T_c (W)

T_c cold temperature (K)

T_H hot temperature (K)

$\dot{W}_i$ power introduced into refrigerator system from external pumps (W)

$\dot{W}$ rate of work (w)

$\dot{W}_{TOTAL}$ total rate of work from all sources (W)

$\Delta\dot{S}_{IRR}$ rate of irreversible entropy production (W/K)

ΔT_c adiabatic temperatures change at cold temperature (K)

η efficiency (dimensionless or %)

σ thermal conductance (W/m^{2}K)

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